CHEMISTRY LETTERS, pp. 247-250, 1974. Published by the Chemical Society of Japan

PREPARATION AND REACTION OF N-BENZIMIDOYLSULFILIMINES1)

Toshio FUCHIGAMI and Keijiro ODO Department of Electric Chemistry, Fuculty of Engineering Tokyo Institute of Technology, Ookayama, Meguro-ku, Tokyo 152

N-Chlorobenzamidine [I] reacted readily with dimethyl sulfide in acetonitrile to form N-benzimidoylaminodimethylsulfonium chloride [II]. Treatment of [II] with sodium hydroxide gave N-benzimidoyl-S,S-dimethylsulfilimine [III] quantitatively. The thermolysis of acyl derivatives of [III] gave rise to 1,2,4-oxadiazoles.

In a continuation of our previous work²⁾³⁾ on the reactions of N-haloamidines, this communication deals with the preparation of sulfonium salt [II] from N-haloamidine and sulfide together with an interesting thermolysis of the acyl derivatives of new type sulfilimine [III] to 1,2,4-oxadiazoles.

Preparation of N-Benzimidoyl-S,S-Dimethylsulfilimine [III]



To a stirred solution of dimethyl sulfide (24 mmol) in acetonitrile (5 ml) was gradually added dropwise a solution of N-chlorobenzamidine (20 mmol) in acetonitrile (5 ml). The temperature was maintained below 15° C during the reaction. After about 0.3 hour of continued stirring active chlorine disappeared and sulfonium salt [II] precipitated. [II] was separated by filtration and washed with acetonitrile, 76~84 % yield, mp 183°C. Recrystallization from ethanol gave a pure product, mp 183~183.5°C (Found : C, 49.27 ; H, 5.76 ; N, 12.90 % . Calcd for $C_9H_{13}N_2SCl$: C, 49.88 ; H, 6.05 ; N, 12.93 %). To a stirred solution of [II] (70 mmol) in water-chloroform (20 ml-70 ml) was added 2N sodium hydroxide (50 ml) below 5° C. After the chloroform layer was separated, residual [III] was extracted twice with 15 ml portions of chloroform. The combined extracts were dried (Na_2SO_4) , filtered, and evaporated under reduced pressure. The residual needles were washed with ether and separated by filtration under nitrogen atmosphere, yield quant, mp $65\sim67^{\circ}$ C. Recrystallization from chloroform - ether gave a pure sulfilimine [III], mp $67\sim68^{\circ}$ C (Found ; N, 15.70 %. Calcd for $C_9H_{12}N_2S$: N, 15.54 %).

[III] is strong hygroscopic crystals and soluble in water and in usual organic solvent except in ether and in hydrocarbons. [III] is quite stable under reflux in THF for 3 hours but decomposes evolving methyl sulfide under reflux in xylene for 2 hours.

The structures of [II] and [III] were discussed on the basis of spectral data. In IR spectra⁴⁾, the C=N stretching vibration of [II] is at 1650 cm⁻¹, while that of [III] is at 1510 cm⁻¹. This shift is analogous to that observed in case of carbonyl group attached to ylid carbon atom or ylid nitrogen atom -----(a).

In UV spectra⁵⁾, [II] and [III] have the same $\lambda \max$ (239 m μ) but $\xi \max$ of [III] (11300) is 2100 larger than that of [II] ----(b).

NMR spectra⁶⁾; [II] : $\delta = 3.03$ (s, $C\underline{H}_3SC\underline{H}_3$), 9.00 (s, N<u>H</u>), 7.40~7.95 (m, $C_6\underline{H}_5$); [III] : $\delta = 2.74$ (s, $C\underline{H}_3SC\underline{H}_3$), 5.50 (s, N<u>H</u>), 7.15~7.95 (m, $C_6\underline{H}_5$)

The resonances of protons to the positively charged sulfur atom and the nitrogen atom are shifted upfield by 0.3 ppm and 3.5 ppm respectively in going from [II] to [III] ---(c).

(a) and (c) suggest that the form [IIIa] is a contributor to the sulfilimine structure.

(b) and (c) suggest that the S-N bond possesses partial double bond character due to 2p-3d orbital overlap [IIIb].

The overall structure can be represented by [K].



248

These resonance forms may contribute to the stabilization of this new sulfilimine. Thermolysis of Acyl Derivatives of [III] ---- Formation of 1,2,4-Oxadiazoles



Acyl derivatives of [III] were easily prepared by the treatment of [III] with The results and physical properties are shown in Table I. acid anhydride.

Compd	R	Yield	Mp	IR Spectra (cm ⁻¹)		Anal (Calcd) %		
		(%)	(°C)	√C=N	-γc=0	C	H	N
IV-a	CH3	60	114~116	1600	1620	59.60 (59.43)	6.01 (6.35)	12.51 (12.60)
I V- Ъ	$\langle \bigcirc$	66	188~190	1570	1600	67.36 (67.58)	5.70 (5.67)	9.70 (9.85)
IV-c C	^H 3-(0)	54	172~173	1550	1590	67.83 (68.43)	6 .13 (6 .08)	9.10 (9.39)

Table I. Physical properties of [IV]

The C=N absorption of [IV] is at shorter wavelength than that of [III], on the other hand, the C=O absorption is at longer wavelength than normal amide absorption. In consideration of these shifts in IR spectra, the structure of [IV] may be represented by [S].

It was expected that 1,2,4-oxadiazole would be formed by the elimination of methyl sulfide. In fact, heating of [IV-b,c] without solvent in test tubes at about 200°C gave rise to 1,2,4-oxadiazoles. However, [IV-a] gave no corresponding product. The structures of these products were confirmed by elemental analysis and IR spectra. The results are shown in Table II.



R	Reaction	Reaction	Yield (%)	Mp	Anal (Calcd) %		
	Temp.(^O C)	Time(min.)	(crude product)	(°C)	C	H	N
$\langle \bigcirc \rangle$	200~210	10	70	108 (108) ⁷	75.74 (75.66)	4.56 (4.54)	12.67 (12.60)
сн3-	190~200	20	63	121 ~122	76.15 (76.25)	5.08 (5.12)	11.49 (11.86)
CH3	160	5	ο	-	-	-	-

Table II. Formation of 1,2,4-Oxadiazoles

The mechanism for this interesting internal ring formation has not been made $clear yet^{8)}$.

References

1)	N-Halo	Compou	inds	of Cy	vanamic	le Derivati	Lves.	III	
	(Part	VXXXIX	of "	Studi	les of	Cyanamide	Deriv	vatives")

- 2) T.Fuchigami, E.Ichikawa, and K.Odo, Bull.Chem.Soc.Japan., 46 1765 (1973).
- 3) T.Fuchigami and K.Odo, Chem.Lett., 917 (1973).
- 4) [II];)NH 3250, 3100 cm⁻¹. [III];)NH 3300 cm⁻¹
- 5) UV spectra were obtained with a Hitachi 624 spectrophotometer using MeOH as solvent.
- 6) NMR spectra were obtained with a Hitachi R-24A spectrometer using TMS as internal standard; s-singlet, m-multiplet. Solvent; [II]: DMSO-d₆ . [II]: CDCl₃
- 7) E.Beckmann and K.Sandel, Ann., 296 285 (1897).
- 8) However, this thermolysis may proceed via nitren in consideration of oxadiazole or isoxazole formation from dimethyl diazidomalonate^{a)} or β-azidovinyl ketones^{b)}.
 - a) R.M.Moriarty, J.M.Kliegman, and C.Shovlin, J.Am.Chem.Soc., 89 5958 (1967).
 - b) S.Maiorana, Ann.Chim.(Rome), <u>56</u>, 1531 (1966).